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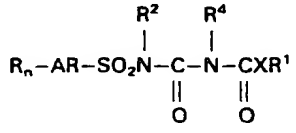
(54) Aryl sulfonylurea carbamates and thiolcarbamates and salts thereof: herbicidal antidotes.

(57) Aryl sulfonylureas as new compositions and included in a two-part herbicide system comprising at least one or more thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide, and as the second part a non-phytotoxic antidotally effective amount of aryl sulfonylurea as an antidote therefor of the formula



in which X is oxygen or sulfur; n is an integer; R is lower alkyl, lower alkylthio, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl;

R^4 is hydrogen, lower alkyl, lower alkoxyalkyl, phenyl and chlorophenyl;

R^2 is hydrogen, lower alkyl, alkoxyalkyl and phenyl;

R^1 is lower alkyl, alkenyl, alkynyl, haloalkyl, alkoxyalkyl, 1-phenylpropenyl, benzyl, chlorobenzyl, haloalkenyl, phenyl and alkyl substituted phenyl; and

AR is phenyl, benzyl, naphthyl, pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts; and organic base salts thereof.

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ARYL SULFONYLUREA CARBAMATES AND THIOLCARBAMATES AND SALTS THEREOF: HERBICIDAL ANTIDOTES

Background of the Invention

While many herbicides are immediately toxic to a large number of weed pests, it is known that the effect of many herbicides upon important plant cultivations is either non-selective or not adequately selective. Thus, many herbicides damage not only the weeds to be controlled, but to a greater or lesser extent, the desirable cultivated plants as well. This holds true for many herbicidal compounds which have been commercially successful and are commercially available. These herbicides include types such as triazines, urea derivatives, halogenated acetanilides; carbamates, thiolcarbamates, thiolcarbamate sulfoxides, pyrrolidinones, and the like. Some examples of these compounds are described in U.S. Patent Nos. 2,891,855, 2,913,237, 3,037,853, 3,175,897, 3,185,720, 3,198,786, 3,442,945, 3,582,314, 3,780,090, 3,952,056 and 4,110,105.

The side effect of injury to a cultivated crop by various herbicides is particularly inconvenient and unfortunate. When used in the recommended amounts in the soil to control broadleaf weeds and grasses, injury such as serious malformation or stunting of the crop plants results in loss of crop yield. The search continues for good selective herbicides.

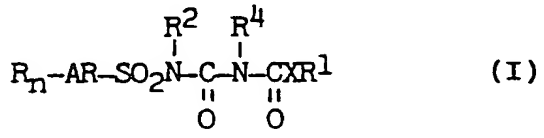
Previous attempts are described to overcome this problem. The treatment of the crop seed with certain "hormonal" antagonistic agents to planting is described, see U.S. Patents 3,131,509 and 3,564,768. The protective agents, as well as the herbicide, in these prior processes are largely specific to certain cultivated plant species or in the nature of the antagonistic agents. The prior antagonistic agents have not been

notably successful. The aforementioned patents specifically exemplify and describe the treatment of seeds employing compounds of a different chemical class not suggestive of the present invention.

Description of the Invention

It has been discovered that cultivated crop plants can be protected against injury by thiolcarbamate-type herbicides, thiolcarbamate sulfoxide-type herbicides, or haloacetanilide-type herbicides and the like, and said injury can be decreased when the thiolcarbamate-type herbicides, thiolcarbamate sulfoxide-type herbicides or haloacetanilide-type herbicides each alone or in mixtures or combination with other compounds, are applied in a variety of ways. Further, as an alternative effect, the tolerance of the crop plants to these herbicides, can be substantially incresed by adding to the soil an antidote compound of the type - aryl sulfonylureas.

Therefore, the present invention also includes a two-part herbicide system consisting essentially of a first-part of one or more herbicides heretofore mentioned, and a second-part of an effective antidote compound therefore, said antidote compounds corresponding to the following formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3 inclusive;

R is lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxy having 1 to 4 carbon atoms, inclusive, lower alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro and lower alkyl sulfonyl;

R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl;

R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2-6 carbon atoms, and phenyl;

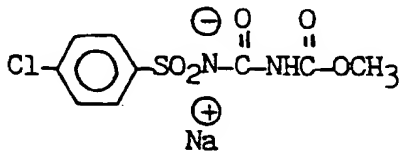
R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive; alkynyl having 3 to 6

carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms inclusive, phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and

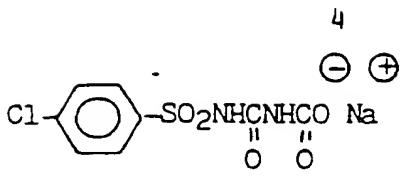
AR is phenyl, benzyl, naphthyl or pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethyl aminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltriallyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine and tribenzylamine.

By the terms "salt" or "salts thereof", it is meant those resulting compounds from the reaction of a compound of this invention and an inorganic or organic base. Inorganic bases include sodium hydroxide, sodium carbonate, potassium carbonate, potassium hydroxide, ammonium hydroxide, phosphonium or sulfonium bases and the like in water, or methanol or ethanol solvents. Organic bases include among others trialkylamines, dibenzylamines, quaternary organic bases, substituted ammonium bases, oxonium bases, other amines including alkyl substituted, alkanol substituted, alkenyl substituted, benzyl substituted, mixed-benzylalkyl substituted diamines, cholines, ammoniums, quinoline, morpholine, hydrazine, and substituted hydrazine, and the like.

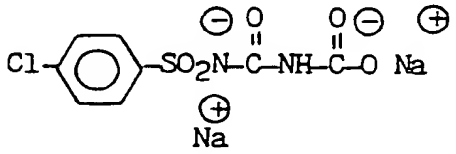
It is recognized that the compounds of this invention have several "acidic" sites for reaction with an inorganic or organic base. Throughout the balance of the application the general nomenclature has been adopted for the sulfonamide salt, for example



or carbamic acid or carbonic acid salt, for example



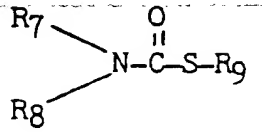
Also recognized is the fact that by using a 2:1 molar equivalent ratio of base to sulfonyl urea a combined or double salt sulfonamide salt and carbamic acid or carbonic acid salt is possible, such as



By way of exemplification, the active thiolcarbamate herbicides employed in the invention may include the following: EPTC, S-ethyl diisobutyl thiolcarbamate, S-propyl dipropyl thiolcarbamate, S-2,3,3,-trichloroallyl diisopropyl thiolcarbamate, S-ethyl cyclohexyl ethyl thiolcarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate, S-4-chlorobenzyl diethyl thiolcarbamate and combinations thereof.

The terms "lower alkyl" and "alkyl" include straight chain and branched chain and cyclic substituents of this group; for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, isopentyl, sec-pentyl, tert-butyl, n-hexyl, isohexyl, cyclopropyl, cyclobutyl, cyclohexyl, and the like; the term "lower alkoxy" includes straight chain and branched chain substituents of this group; for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, sec-butoxy, sec-pentoxy, tert-butoxy, n-hexoxy, isohexoxy and the like; the term "alkynyl" includes substituents of this type having straight or branched chain and at least one triple bond; for example, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 1-hexynyl, 3-hexynyl and the like; and the term "alkenyl" includes substituents of this group having a straight or branched chain configuration and at least one double bond; for example, allyl, methallyl, ethallyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-methyl-1-butenyl, 2-methyl-3-butenyl, 1-pentenyl, 2-pentenyl, 2-methyl-1-pentenyl and the like. The term "halo" includes those substituents as, chloro, bromo, iodo and fluoro as mono, di, tri or tetra substituents and combinations thereof.

By thiolcarbamate herbicides the present invention includes compounds of the formula



in which

R_7 is selected from the group consisting of alkyl 1 to 6 carbon atoms and alkenyl 2 to 6 carbon atoms;

R_8 is selected from the group consisting of alkyl 1 to 6 carbon atoms, alkenyl 2 to 6 carbon atoms, cyclohexyl, phenyl and benzyl; or

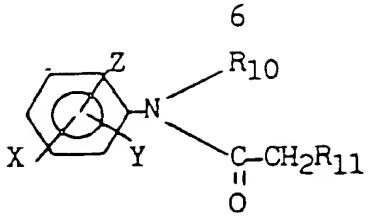
R_7 and R_8 taken together with the nitrogen atom to which they are attached form an alkylene ring substituted and unsubstituted 2 to 9 carbon atoms; and

R^9 is selected from the group consisting of alkyl 1 to 6 carbon atoms, haloalkyl 1 to 6 carbon atoms, alkenylene ring 5 to 10 carbon atoms, phenyl, substituted phenyl, benzyl and substituted benzyl.

By thiolcarbamate sulfoxide-type herbicides are those thiolcarbamate herbicides mentioned herein which have been oxidized by methods as disclosed and described in U.S. Patents 3,897,492, 3,986,168, 3,896,169, U.S. 3,989,684 and which are incorporated herein by reference.

By way of exemplification, active thiolcarbamate sulfoxide herbicides employed in the present invention may include the following: S-ethyl dipropyl thiolcarbamate sulfoxide, S-ethyl diisobutyl thiolcarbamate sulfoxide, S-propyl dipropyl thiolcarbamate sulfoxide, S-2,3,3-trichloroalkyl diisopropyl thiolcarbamate sulfoxide, S-ethyl hexahydro-1H-azepine-1-carbothioate sulfoxide, S-4-chlorobenzyl diethyl thiolcarbamate sulfoxide and combinations thereof.

By haloacetanilide herbicides the present invention includes compounds of the formula



in which

X, Y and Z are independently selected from the group consisting of hydrogen, alkyl 1 to 4 carbon atoms and alkoxy 1 to 4 carbon atoms;

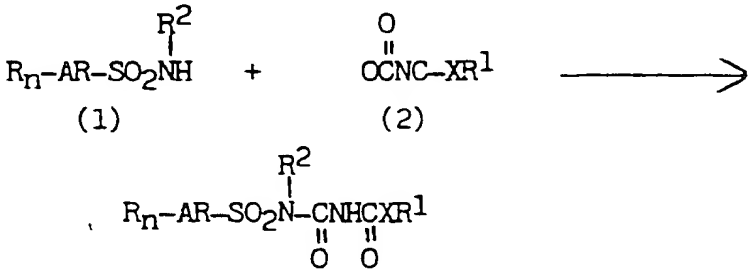
R_{10} is selected from the group consisting of alkyl 1 to 6 carbon atoms, alkylalkoxy 2 to 10 carbon atoms, acetoxy 2 to 6 carbon atoms and dioxane; and

R_{11} is selected from the group consisting of chlorine, bromine and iodine.

By way of exemplification, active haloacetanilide herbicides employed in the invention may include the following: 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, 2-chloro-2'-methyl,6'-ethyl-N-(methoxypropyl)-(2) acetanilide, 2-chloro-2',6'-dimethyl-N-(methoxymethyl) acetanilide, 2-chloro-2'methyl,6'-ethyl-N-(ethoxymethyl) acetanilide, 2-chloro-N-isopropyl acetanilide, 2-chloro-2',6'-diethyl-N-(n-butoxymethyl) acetanilide, and 2-chloro-N-carbethoxymethyl-2',6'-diethyl acetanilide.

In general, the active antidote compounds of the present invention can be prepared by the following methods.

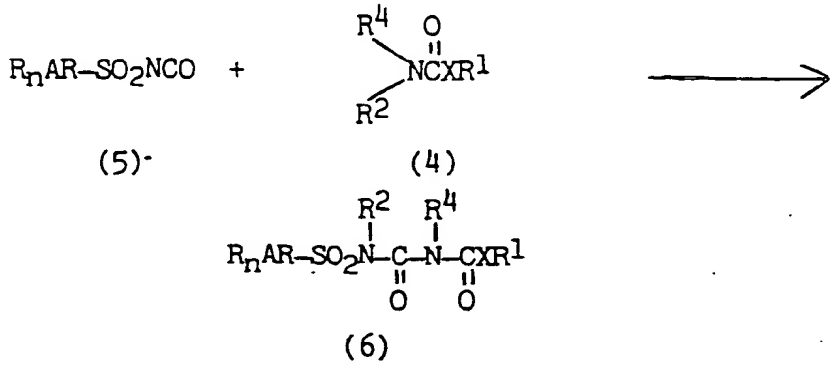
I. An appropriate substituted aryl sulfonamide (1) is reacted with a substituted carbamoyl or thiocarbamoyl isocyanate (2) to produce the substituted aryl sulfonylurea (3). This reaction is depicted by following equation:



(1) (2)

(3)

II. An alternative reaction is the reaction of a substituted carbamate or thiolcarbamate (4) with a substituted aryl sulfonyl isocyanate (5) to produce the substituted aryl sulfonylurea (6). This reaction is depicted by the following equation:



(5) (4)

(6)

wherein R, AR, R^1 and n have the same significance as previously defined.

In reaction schemes I and II, the starting material intermediates are well-known in the prior art and the reactions described in I and II are performed in the presence of an organic solvent, such as toluene and the like, where good chemical practice dictates. The reactions are either exothermic as in II or heat can be applied as in I. The reaction temperatures can vary between about -20°C to about 150°C or the reflux temperature of the reaction mixture. The reaction pressure may be atmospheric, subatmospheric or superatmospheric. However, for convenience of conducting the reactions, the pressure is generally atmospheric. The reaction time will, of course vary depending upon the reactants and reaction temperature. Generally, the reaction time is from 0.25 to 24 hours depending upon the steps and rate of reaction. After the reaction is complete, the product is recovered by separation from the by-products and the solvent removed, as by filtration or evaporation or distillation. The structure is confirmed by nuclear magnetic resonance or infrared spectroscopy.

This invention relates to compounds having the formula I

$$R_n\text{-AR-SO}_2\text{-N}(R^2)\text{-C}(=O)\text{-N}(R^4)\text{-CXR}^1 \qquad (I)$$

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive;

R is lower alkyl having 1 to 4 carbon atoms, inclusive; lower alkoxy having 1 to 4 carbon atoms; lower alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl;

R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl;

R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2-6 carbon atoms, and phenyl;

R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and

AR is phenyl, benzyl, naphthyl, pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine and tribenzylamine.

Preferred compounds are:

1) compounds according to formula I in which R is halogen, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

2) compounds according to point 1 in which R is 4-chloro, and n is 1,

3) compounds according to point 2 in which R^1 is methyl,

4) compounds according to point 2 in which R^1 is ethyl,

5) compounds according to point 2 in which R^1 is tertiary butyl,

6) compounds according to point 2 in which R^1 is isopropyl,

7) compounds according to point 1 in which R is 2,5-dichloro, n is 2 and R^1 is methyl,

8) compounds according to point 1 in which R is 2-chloro, n is 1 and R^1 is methyl,

9) compounds according to formula I in which n is O, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

10) compounds according to point 9 in which R^1 is n-butyl,

11) compounds according to point 9 in which R^1 is methyl,

12) compounds according to formula I in which R is lower alkyl, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

13) compounds according to point 12 in which R is 4-methyl, n is 1 and R^1 is methyl,

14) compounds according to point 12 in which R^1 is ethyl,

15) compounds according to point 12 in which R^1 is isopropyl,

16) compounds according to point 12 in which R^1 is tertiary butyl,

17) compounds according to point 12 in which R is 2-methyl, n is 1 and R^1 is methyl,

18) compounds according to formula I in which R is trifluoromethyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

19) compounds according to point 18 in which R is 3-trifluoromethyl and R^1 is methyl,

20) compounds according to formula I in which R is nitro, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

21) compounds according to point 20 in which R is 3-nitro and R^1 is methyl,

22) compounds according to point 20 in which R is 4-nitro and R^1 is methyl,

23) compounds according to formula I in which R is lower alkylthio, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

24) compounds according to point 23 in which R is 4-methylthio and R^1 is methyl,

25) compounds according to formula I in which R is lower alkoxy, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

26) compounds according to point 25 in which R is 4-methoxy and R^1 is methyl,

27) compounds according to formula I in which R is lower alkyl sulfonyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

28) compounds according to point 27 in which R is 4-methyl-sulfonyl and R^1 is methyl,

29) compounds according to formula I in which n is O, AR is benzyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

30) compounds according to point 29 in which R^1 is methyl,

31) compounds according to formula I in which R is lower alkyl, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

32) compounds according to point 31 in which R is 4-methyl, R^4 is methyl and R^1 is methyl,

33) compounds according to point 31 in which R is 4-methyl, R^4 is ethyl and R^1 is methyl,

34) compounds according to formula I in which R is halogen, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

35) compounds according to point 34 in which R is 4-chloro, R^4 is methyl and R^1 is methyl,

36) compounds according to point 34 in which R is 4-chloro, R^4 is ethyl and R^1 is methyl,

37) compounds according to formula I in which n is O, AR is 2-pyridyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

38) compounds according to point 37 in which R^1 is methyl,

39) compounds according to formula I in which n is O, AR is 2-naphthyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

40) compounds according to point 39 in which R^1 is methyl,

41) compounds according to formula I in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic bases selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine,

42) compounds according to point 41 wherein the compound is the sodium sulfonamide salt,

43) compounds according to point 41 wherein the compound is the sodium carbamic acid salt,

44) compounds according to point 41 wherein the compound is the disodium sulfonamide - carbamic acid double salt,

45) compounds according to point 41 wherein the compound is the potassium sulfonamide salt, potassium carbamic acid salt or dipotassium sulfonamide - carbamic acid double salt,

46) compounds according to point 41 wherein the compound is the ammonium sulfonamide salt, ammonium carbamic acid salt or diammonium sulfonamide - carbamic acid double salt,

47) compounds according to point 41 wherein the compound is the triethylammonium sulfonamide salt, triethylammonium carbamic acid salt, or di-triethylammonium sulfonamide - carbamic acid double salt,

48) compounds according to point 41 wherein the compound is a quaternary ammonium sulfonamide salt, a quaternary ammonium carbamic acid salt or a di-quaternary ammonium sulfonamide - carbamic acid double salt.

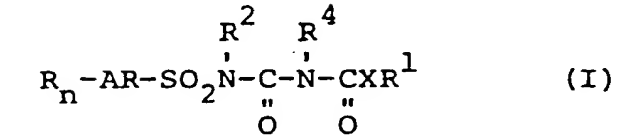
This invention relates also to a method of protecting a crop from injury due to at least one thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide, comprising

a) applying to the crop seed prior to planting, a non-phytotoxic antidotally effective amount of a compound corresponding to the following formula I; or

b) preplant incorporation in the soil in which said crop is to be planted, a non-phytotoxic antidotally effective amount of a compound of the formula I; or

c) applying in-furrow to the seed and soil in which said crop is to be planted, a non-phytotoxic antidotally

effective amount of a compound corresponding to the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive; R is lower alkyl having 1 to 4 carbon atoms; inclusive; lower alkoxy having 1 to 4 carbon atoms; lower alkylthio having 1 to 4 carbon atoms, inclusive; halogen, trifluormethyl, cyano, nitro, lower alkyl sulfonyl; R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive; lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl; R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2 to 6 carbon atoms, and phenyl; R^1 is lower alkyl havin 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive; haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive; 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive; phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and AR is phenyl, benzyl, naphthyl, pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic base salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenmediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N,-dialkyl hydrazine, morpholine, and tribenzylamine.

Preferred methods are methods in which the following compounds are used:

1) of the formula I in which R is halogen, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

2) compounds as mentioned under point 1 in which R is 4-chloro and n is 1,

3) compounds as mentioned under point 1 in which R^1 is methyl,

4) compounds as mentioned under point 1 in which R^1 is ethyl,

5) compounds as mentioned under point 1 in which R^1 is tertiary butyl,

6) compounds as mentioned under point 1 in which R^1 is isopropyl,

7) compounds as mentioned under point 1 in which R is 2,5-dichloro, n is 2 and R^1 is methyl,

8) compounds as mentioned under point 1 in which R is 2-chloro, n is 1 and R^1 is methyl,

9) compounds of the formula I in which n is 0, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

10) compounds of the formula I in which R is lower alkyl, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

11) compounds of the formula I in which R is trifluoromethyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

12) compounds of the formula I in which R is nitro, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

13) compounds of the formula I in which R is lower alkylthio, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

14) compounds of the formula I in which R is lower alkoxy, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

15) compounds of the formula I in which R is lower alkyl sulfonyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

16) compounds of the formula I in which n is O, AR is benzyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

17) compounds of the formula I in which R is lower alkyl, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

18) compounds of the formula I in which R is halogen, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen, and R^1 is lower alkyl,

19) compounds of the formula I in which n is O, AR is 2-pyridyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

20) compounds of the formula I in which n is O, AR is 2-naphthyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

21) compounds of the formula I in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group, said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic base sals selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine,

22) compounds as mentioned under point 21 wherein the compound is the sodium sulfonamide salt,

23) compounds as mentioned under point 21 wherein the compound is the sodium carbamic acid salt,

24) compounds as mentioned under point 21 wherein the compound is the disodium sulfonamide - carbamic acid double salt,

25) compounds as mentioned under point 21 wherein the compound is the potassium sulfonamide salt, potassium carbamic acid salt or dipotassium sulfonamide - carbamic acid double salt,

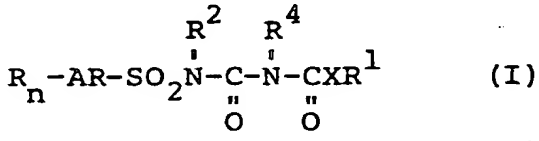
26) compounds as mentioned under point 21 wherein the compound is the ammonium sulfonamide salt, ammonium

carbamic acid salt or a diammonium sulfonamide - carbamic acid double salt,

27) compounds as mentioned under point 21 wherein the compound is the triethylammonium sulfonamide salt, triethylammonium carbamic acid salt, or a di-triethylammonium sulfonamide - carbamic acid double salt,

28) compounds as mentioned under point 21 wherein the compound is a quaternary ammonium sulfonamide salt, a quaternary ammonium carbamic acid salt or a di-quaternary ammonium sulfonamide - carbamic acid double salt.

This invention relates also to a herbicidal composition comprising at least one thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide active herbicide and an antidotally effective amount of a compound therefore corresponding to the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive, R is lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxy having 1 to 4 carbon atoms; lower alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl acylamido; R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorphenyl; R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having from 2 to 6 carbon atoms, and phenyl; R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, in-

clusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and AR is phenyl, benzyl, naphthyl, pyridyl, or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

Preferred herbicidal compositions comprise compounds

1) of the general formula I in which R is halogen, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

2) as mentioned under point 1 in which R is 4-chloro and n is 1,

3) as mentioned under point 1 in which R^1 is methyl,

4) as mentioned under point 1 in which R^1 is ethyl,

5) as mentioned under point 1 in which R^1 is tertiary butyl,

6) as mentioned under point 1 in which R^1 is isopropyl,

7) as mentioned under point 1 in which R is 2,5-dichloro, n is 2 and R^1 is methyl,

8) as mentioned under point 1 in which R is 2-chloro, n is 1 and R^1 is methyl,

9) of the general formula I in which n is 0, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

10) of the general formula I in which R is lower alkyl, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is loweralkyl,

11) of the general formula I in which R is trifluoromethyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

12) of the general formula I in which R is nitro, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

13) of the general formula I in which R is lower alkylthio, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

14) of the general formula I in which R is lower alkoxy, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

15) of the general formula I in which R is lower alkyl sulfonyl, n is 1, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

16) of the general formula I in which n is 0, AR is benzyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

17) of the general formula I in which R is halogen, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

18) of the general formula I in which R is halogen, n is 1, AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

19) of the general formula I in which n is 0, AR is 1-pyridyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

20) of the general formula I in which n is 0, AR is 2-naphthyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl,

21) of the general formula I in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group, said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic base salts selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine,

22) as mentioned under point 21 wherein the compound is the sodium sulfonamide salt,

23) as mentioned under point 21 wherein the compound is the sodium carbamic acid salt,

24) as mentioned under point 21 wherein the compound is the disodium sulfonamide - carbamic acid double salt,

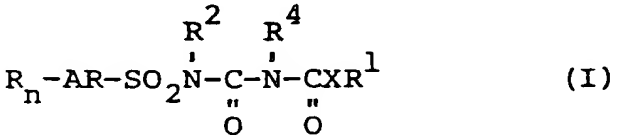
25) as mentioned under point 21 wherein the compound is the potassium sulfonamide salt, potassium carbamic acid salt or dipotassium sulfonamide - carbamic acid double salt,

26) as mentioned under point 21 wherein the compound is the ammonium sulfonamide salt, ammonium carbamic salt or di-ammonium sulfonamide - carbamic acid double salt,

27) as mentioned under point 21 wherein the compound is the triethylammonium sulfonamide salt, triethylammonium carbamic acid salt, or a di-triethylammonium sulfonamide-carbamic acid double salt,

28) as mentioned under point 21 wherein the compound is a quaternary ammonium sulfonamide salt, a quaternary ammonium carbamic acid salt or a di-quaternary ammonium sulfonamide - carbamic acid double salt.

This invention relates also to a method of increasing the resistance of crop plant seed to injury from at least one herbicidally active thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide, comprising applying to the surface of said seed a coating of an antidotally effective, but substantially non-phytotoxic amount of a compound corresponding to the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3 inclusive; R is lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxy having 1 to 4 carbon atoms; lower

alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl; R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl; R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2 to 6 carbon atoms, and phenyl; R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, alkyl having 1 to 4 carbon atoms, inclusive, substituted phenyl; and AR is phenyl, benzyl, naphthyl, pyridyl, or styryl; and the inorganic base salts sodium potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

A preferred method is the method of protecting soybean plants from injury due to at least one thiolcarbamate or haloacetanilide comprising applying to the soil the herbicidal composition as mentioned above.

In a preferred method the thiolcarbamate herbicide compound is selected from EPTC, S-ethyl diisobutyl thiolcarbamate, S-propyl dipropyl thiolcarbamate, S-2,3,3,-trichloroallyl diisopropyl thiolcarbamate, S-ethyl cyclohexyl ethyl thiolcarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate, S-4-chlorobenzyl diethyl thiolcarbamate and combinations thereof.

This invention relates also to a herbicidal composition comprising an active thiolcarbamate, thiolcarbamate sulfoxide, or haloacetanilide herbicide compound and a non-phytotoxic antidotally effective amount of a carbamate or thiolcarbamate of an aryl sulfonylurea, having 5 to 12 carbon atoms, inclusive, said carbamate or thiolcarbamate being antidotally active with said herbicide compounds.

This invention relates also to a herbicidal composition comprising an active thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide compound and a non-phytotoxic, antidotally effective amound of an inorganic or organic salt of a carbamate or thiolcarbamate of an aryl sulfonylurea, having 5 to 12 carbon atoms, inclusive, said salt being antidotally active with said herbicide compound.

Especially preferred compounds of this invention are:

A) compounds of the general formula I in which R is lower alkyl, lower alkoxy, alkylthio, halogen, trifluoromethyl, cyano, nitro or lower alkylsulfonyl and AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl, alkenyl, alkynyl, haloalkyl, haloalkenyl, or alkoxyalkyl,

B) compounds of the general formula I in which R is lower alkyl, lower alkoxy, alkylthio, halogen, trifluoromethyl, cyano, nitro, or lower alkyl sulfonyl and AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is benzyl, chlorobenzyl, phenyl, alkyl substituted phenyl or 1-phenyl propenyl,

C) compounds of the general formula I in which R is lower alkyl, lower alkoxy, alkylthio, halogen, trifluoromethyl cyano, nitro or lower alkylsulfonyl and AR is phenyl, R^4

is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is alkyl, alkenyl, alkynyl, haloalkyl, haloalkenyl, or alkoxyalkyl,

D) compounds of the general formula I in which R is lower alkyl, lower alkoxy, alkylthio, halogen, trifluoromethyl, cyanao, nitro, or lower alkyl sulfonyl and AR is phenyl, R^4 is lower alkyl, R^2 is hydrogen, X is oxygen and R^1 is benzyl, chlorobenzyl, phenyl, alkyl substituted phenyl or 1-phenyl propenyl.

The compounds of the present invention and their preparation are more particularly illustrated by the following examples. Following the examples of preparation is a table of compounds which are prepared according to the procedures described herein. Compound numbers have been assigned to them and are used for identification throughout the balance of the specification.

Example 1

Preparation of 1-(4'-chlorobenzenesulfonyl)-3-methoxycarbonyl urea

Methyl carbamate (43.0 grams, 0.57 moles) was stirred in 500 milliliters of dry toluene. 4-chlorobenzenesulfonyl isocyanate (125 grams, 0.57 moles) was added dropwise. An exothermic reaction occurred. The reaction mixture was kept at 80°C for 1 1/2 hours. It was then cooled and the percipitate removed by filtration. The filtered material was washed with toluene and dried. There was obtained 159 grams of the title product, m.p. 174-175°C.

Example 2

Preparation of 1-(4'-nitrobenzenesulfonyl)-3-methoxycarbonyl urea

To 4-nitrobenzenesulfonamide (2.1 grams, 0.01 mole) in 100 milliliters dry toluene was added 1.2 grams (0.012 mole) methoxycarbonyl isocyanate. Three drops of pyridine were added. The mixture was refluxed for four hours. After cooling the precipitate was filtered off and washed with toluene. The solid material was dried. There was obtained 2.4 grams of the title compound, m.p. 150-158°C.

Example 3

Preparation of salts

Sodium salts of 1-(4'-chlorobenzenesulfonyl)-3-methoxy carbonyl urea

A. One equivalent weight of sodium hydroxide was added to one equivalent weight of 1-(4'-chlorobenzenesulfonyl)-3-methoxy carbonyl urea in aqueous solution. There was obtained at room temperature the monosodium carbamic acid salt of the starting compound.

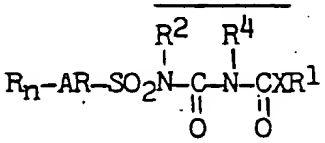
B. One mole of 1-(4'-chlorobenzenesulfonyl)-3-methoxy carbonyl urea was added to one mole of sodium hydroxide in 5% methanol solution. This was stirred while cooling in an ice-water bath. The solvent was evaporated. There was obtained a white crystalline product, the sodium sulfonamide salt of the starting compound, m.p. 220-221°C.

C. In a similar manner as B potassium hydroxide in methanol was reacted with 1-(4'-chlorobenzenesulfonyl)-3-methoxy carbonyl urea. The potassium sulfonamide salt was prepared and isolated, m.p. 75-85°C.

D. In a similar manner as B, triethylamine in methanol was reacted with the compound from Example 1. The triethylamine sulfonamide salt was prepared and isolated, m.p. 100-113°C.

E. In a similar manner as B, ammonium hydroxide in methanol was reacted with the compound from Example 1. The ammonium sulfonamide salt was prepared and isolated, m.p. 92-98°C.

TABLE I



Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
1	4-Cl	phenyl	H	S	$n-C_4H_9$	H	88-92°C
2	-	phenyl	H	O	CH_3	H	semi-solid*
3	4-Cl	phenyl	H	O	CH_3	H	174-175°C
4	4-Cl	phenyl	H	O	C_2H_5	H	104-107°C
5	4-Cl	phenyl	H	O	$t-C_4H_9$	H	96-100°C
6	4-Cl	phenyl	H	O	$i-C_3H_7$	H	82-95°C
7	$4-CH_3$	phenyl	H	O	CH_3	H	138-140°C
8	$4-CH_3$	phenyl	H	O	C_2H_5	H	156-157
9	$4-CH_3$	phenyl	H	O	$i-C_3H_7$	H	140-142°C
10	$4-CH_3$	phenyl	H	O	$t-C_4H_9$	H	123-125°C
11	$3-CF_3$	phenyl	H	O	CH_3	H	waxy-solid*
12	2,5-di Cl	phenyl	H	O	CH_3	H	123-133°C
13	-	2-pyridyl	H	O	CH_3	H	183-185°C
14	-	2-naphthyl	H	O	CH_3	H	154-164°C
15	2-Cl	phenyl	H	O	CH_3	H	semi-solid*
16	$3-NO_2$	phenyl	H	O	CH_3	H	151-154°C
17	$4-NO_2$	phenyl	H	O	CH_3	H	150-158°C
18	$4-CH_3S$	phenyl	H	O	CH_3	H	147-155°C
19	$4-CH_3O$	phenyl	H	O	CH_3	H	155-158°C
20	$2-CH_3$	phenyl	H	O	CH_3	H	137-142°C
21	$4-CH_3SO_2$	phenyl	H	O	CH_3	H	semi-solid*
22	-	benzyl	H	O	CH_3	H	155-160°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
23	4-CH_3	phenyl	CH_3	O	CH_3	H	104-113°C
24	4-Cl	phenyl	CH_3	O	CH_3	H	128-133°C
25	4-CH_3	phenyl	C_2H_5	O	CH_3	H	101-107°C
26	4-Cl	phenyl	C_2H_5	O	CH_3	H	75-95°C
27	4-Cl	phenyl	H	O	CH_3	sulfonamide sodium salt solution	130-135°C
28	4-Cl	phenyl	H	O	CH_3	sulfonamide sodium salt	220-221°C
29	4-Cl	phenyl	H	O	Na^+ Double salt	H	>300°C
30	4-Cl	phenyl	H	O	CH_3	sulfonamide potassium salt	75-85°C
31	4-Cl	phenyl	H	O	CH_3	sulfonamide triethylamine salt	100-113°C
32	4-Cl	phenyl	H	O	CH_3	sulfonamide ammounium salt	92-98°C
33	4-Cl	phenyl	H	O	CH_3	sulfonamide tributylamine salt	viscous liquid
34	4-Cl	phenyl	H	O	CH_3	sulfonamide dibenzylamine salt	145-150°C
35	4-Cl	phenyl	H	O	Na^+	carbamic acid sodium salt	
36	4-Cl	phenyl	H	S	CH_3	H	171-181°C
37	4-CH_3	phenyl	H	S	CH_3	H	181-187°C
38	2,5-di CH_3	phenyl	H	O	CH_3	H	115-125°C
39	3,4-di Cl	phenyl	H	O	CH_3	H	164-168°C
40	2-NO_2	phenyl	H	O	CH_3	H	143-159°C
41	4-Br	phenyl	H	O	CH_3	H	181-187°C
42	3,5-di Cl	phenyl	H	O	CH_3	H	194-195°C
43	4-F	phenyl	H	O	CH_3	H	157-160°C
44	3-Cl	phenyl	H	O	CH_3	H	140-141°C
45	4-NO_2	phenyl	H	O	$CH_3OCH_2CH_2$-	H	130-134°C
46	4-CH_3	phenyl	H	O	CH_3	H	semi-solid*
47	4-Cl	phenyl	H	O	$CH_3OCH_2CH_2$-	H	semi-solid*
48	4-CH_3	phenyl	H	O	benzyl	H	165-169°C
49	4-CH_3	phenyl	H	O	CH_2=$CHCH_2$	H	126-130°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
50	4-Cl	phenyl	H	O	benzyl	H	176-179°C
51	4-Cl	phenyl	H	O	$CH_2=CHCH_2-$	H	122-125°C
52	4-NO_2	phenyl	H	O	C_2H_5	H	183-185°C
53	4-NO_2	phenyl	C_2H_5	O	CH_3	H	128-131°C
54	4-Cl	phenyl	i-C_3H_7	O	CH_3	H	85-92°C
55	4-Cl	phenyl	n-C_3H_7	O	CH_3	H	semi-solid*
56	4-Cl	phenyl	phenyl	O	CH_3	H	semi-solid*
57	4-Cl	phenyl	4-Cl-phenyl	O	CH_3	H	123-129°C
58	4-Cl	phenyl	$CH_3OCH_2CH_2$	O	CH_3	H	liquid*
59	4-NO_2	phenyl	$CH_3OCH_2CH_2$	O	CH_3	H	liquid*
60	4-Cl	phenyl	H	O	CH_3	CH_3	semi-solid*
61	4-NO_2	phenyl	H	O	CH_3	phenyl	107-110°C
62	4-Cl	phenyl	H	O	CH_3	CH_3	semi solid*
63	4-CH_3	phenyl	H	O	$CH\equiv CCH_2-$	H	155-158°C
64	4-CH_3	phenyl	H	O	$CH_3C\equiv CCH_2-$	H	147-154°C
65	4-Cl	phenyl	CH_3	O	CF_3H_2-	H	83-86°C
66	3-Cl	phenyl	H	O	C_2H_5	H	137-130°C
67	3-Cl	phenyl	H	O	i-C_3H_7	H	140-141°C
68	3-Cl	phenyl	H	O	$(CH_3)_2CHCH_2-$	H	102-104°C
69	3-Cl	phenyl	H	O	$CH_3OCH_2CH_2-$	H	slurry*
70	3-Cl	phenyl	H	O	$(CH_2)_2OCH_2CH_2-$	H	n_D^{30} = 1.5084
71	4-Cl	phenyl	C_2H_5	S	CH_3	H	semi-solid*
72	4-NO_2	phenyl	H	O	phenyl	H	161-166°C
73	4-CF_3	phenyl	H	O	CH_3	H	158-159°C
74	4-CF_3	phenyl	H	O	C_2H_5	H	152-153°C
75	4-CF_3	phenyl	H	O	i-C_3H_7	H	160-161°C
76	4-CF_3	phenyl	H	O	i-C_4H_9	H	150-152°C
77	4-NO_2	phenyl	H	O	benzyl	H	170-173°C
78	4-Cl	phenyl	H	O	CH_3	$CH_3OCH_2CH_2-$	slurry
79	—	1-naphthyl	H	O	CH_3	H	136-139°C
80	4-Cl	phenyl	H	O	$CH_3C\equiv CCH_2-$	H	120-123°C
81	4-NO_2	phenyl	H	O	$CH_2=CHCH_2-$	H	158-162°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
82	4-NO_2	phenyl	H	O	$CH_3C{\equiv}CCH_2$-	H	170-172°C
83	4-CF_3	phenyl	H	O	$CH_3OCH_2CH_3$	H	112-113°C
84	4-CF_3	phenyl	H	O	i-$C_3H_7OCH_2CH_2$-	H	soft solid*
85	4-Cl	phenyl	H	O	CH_3	sulfonamide aniline salt	79-82°C
86	4-Cl	phenyl	H	O	CH_3	sulfonamide p-toluidine salt	128-129°C
87	4-Cl	phenyl	H	O	CH_3	sulfonamide benzylamine salt	153-154°C
88	4-Cl	phenyl	H	O	CH_3	sulfonamide allylamine salt	154-155°C
89	4-Cl	phenyl	H	O	CH_3	sulfonamide diallylamine salt	118-121°C
90	4-Cl	phenyl	H	O	CH_3	sulfonamide di-ethylamino propylamine salt	134-136°C
91	4-Cl	phenyl	H	O	CH_3	sulfonamide ethanol amine salt	1.5421
92	4-Cl	phenyl	H	O	CH_3	sulfonamide quinoline salt	75-85°C
93	4-Cl	phenyl	H	O	CH_3	sulfonamide triethanol-amine salt	1.5410
94	4-Cl	phenyl	H	O	CH_3	sulfonamide diethylamino ethanol salt	1.5292
95	4-Cl	phenyl	H	O	CH_3	sulfonamide methylamine salt	152-154°C
96	4-Cl	phenyl	H	O	CH_3	sulfonamide ethylamine salt	126-128°C
97	4-Cl	phenyl	H	O	CH_3	sulfonamide diethylamine salt	54-62°C
98	4-Cl	phenyl	H	O	CH_3	sulfonamide n-propylamine salt	159-163°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
99	4-Cl	phenyl	H	O	CH_3	sulfonamide i-propylamine salt	104-108°C
100	4-Cl	phenyl	H	O	CH_3	sulfonamide diisopropyl-amine salt	128-131°C
101	4-Cl	phenyl	H	O	CH_3	sulfonamide hydrazine salt	72-78°C
102	4-Cl	phenyl	H	O	CH_3	sulfonamide N,N-dimethyl hydrazine salt	61-64°C
103	4-Cl	phenyl	H	O	CH_3	sulfonamide ethylene diamine bis-salt	184-186°C
104	4-Cl	phenyl	H	O	CH_3	sulfonamide ethylamino ethyl amine salt	69-76°C
105	4-Cl	phenyl	H	O	CH_3	sulfonamide tetraethyl ammonium salt	46-49°C
106	4-Cl	phenyl	H	O	CH_3	sulfonamide tetrabutyl ammonium salt	99-102°C
107	4-Cl	phenyl	H	O	CH_3	sulfonamide isoquinoline salt	92-98°C
108	4-Cl	phenyl	H	O	CH_3	sulfonamide diethanolamine salt	42-47°C
109	4-Cl	phenyl	H	O	CH_3	sulfonamide morpholine salt	156-158°C
110	4-Cl	phenyl	H	O	CH_3	sulfonamide tribenzylamine salt	91-95°C
111	4-Cl	phenyl	H	O	CH_3	sulfonamide choline salt	1.5250
112	4-Cl	phenyl	H	O	CH_3	sulfonamide hexadecyl tri-methyl ammonium salt	84-87°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
113	4-Cl	phenyl	H	O	CH_3	sulfonamide benzyltrimethyl ammonium salt	semi-solid*
114	4-Cl	phenyl	H	O	CH_3	sulfonamide triethylphenyl ammonium salt	semi-solid*
115	4-Cl	phenyl	H	O	$CH{\equiv}CCH_2-$	H	135-140°C
116	4-Cl	phenyl	H	O	CH_3	sulfonamide triallylamine salt	1.5354
117	3-NO_2, 4-Cl	phenyl	H	O	CH_3	H	149-154°C
118	4-NO_2	phenyl	CH_3	O	CH_3	H	145-150°C
119	4-Cl	phenyl	CH_3	O	$CH_2{=}CHCH_2-$	H	64-66°C
120	4-Cl	phenyl	CH_3	O	$CH{\equiv}CCH_2$	H	150-154°C
121	4-NO_2	phenyl	CH_3	O	CH_3	H	98-101°C
122	4-NO_2	phenyl	CH_3	O	C_2H_5	H	99-103°C
123	4-Cl	phenyl	CH_3	O	C_2H_5	H	62-66°C
124	4-Cl	phenyl	C_2H_5	O	C_2H_5	H	69-74°C
125	4-NO_2	phenyl	C_2H_5	O	C_2H_5	H	99-101°C
126	4-Cl	phenyl	CH_3	O	$CH_3C{\equiv}CCH_2-$	H	83-89°C
127	4-CH_3	phenyl	CH_3	O	benzyl	H	84-91°C
128	4-CH_3	phenyl	CH_3	O	$CH_2{=}CHCH_2-$	H	50-57°C
129	4-CH_3	phenyl	CH_3	O	$CH{\equiv}CCH_2$	H	154-158°C
130	4-CH_3	phenyl	CH_3	O	$CH_3C{\equiv}CCH_2-$	H	100-110°C
131	4-NO_2	phenyl	CH_3	O	benzyl	H	136-139°C
132	4-NO_2	phenyl	H	O	CH_3	sulfonamide choline salt	52-58°C
133	4-CH_3	phenyl	C_2H_5	O	$CH_2{=}CHCH_2-$	H	1.5258
134	4-CH_3	phenyl	C_2H_5	O	$CH{\equiv}CCH_2-$	H	75-80°C
135	4-CH_3	phenyl	C_2H_5	O	$CH_3C{\equiv}CCH_2$	H	85-92°C
136	4-Cl	phenyl	C_2H_5	O	$CH_2{=}CHCH_2-$	H	1.5336
137	4-Cl	phenyl	C_2H_5	O	$CH{\equiv}CCH_2-$	H	95-100°C
138	4-Cl	phenyl	C_2H_5	O	$CH_3C{\equiv}CCH_2-$	H	waxy-solid
139	4-CH_3	phenyl	H	O	$CH_2{=}C(CH_3)CH_2-$	H	132-3
140	4-Cl	phenyl	CH_3	O	$CH_2{=}C(CH_3)CH_2-$	H	81-88°C

TABLE I (continued)

Com. No.	R_n	AR	R^4	X	R^1	R_2	Physical Constant m.p. or n_D^{30}
141	4-Cl	phenyl	H	O	$CH_3CH=CHCH_2-$	H	72-77°C
142	4-CH_3	phenyl	H	O	CH_2ClCH_2-	H	118-121°C
143	4-Cl	phenyl	H	O	CH_2ClCH_2-	H	102-112°C
144	4-CH_3	phenyl	C_2H_5	O	$CH_2=C(CH_3)CH_2-$	H	1.5090
145	4-Cl	phenyl	H	O	$CH_2=C(CH_3)CH_2-$	H	149-152°C
146	4-Cl	phenyl	$-CH_2CH=CH_2$	O	CH_3	H	1.5388
147	4-CH_3	phenyl	H	O	$CH_3CH=CHCH_2-$	H	52-60°C
148	4-CH_3	phenyl	CH_3	O	$(CH_3)_3CCH_2-$	H	94-97°C
149	4-CH_3	phenyl	CH_3	O	$HC\equiv CCH(phenyl)-$	H	1.5533
150	4-CH_3	phenyl	H	O	$(CH_3)_3CCH_2-$	H	83-91°C
151	4-CH_3	phenyl	C_2H_5	O	$(CH_3)_3CCH_2-$	H	102-106°C
152	4-CH_3	phenyl	H	O	$CH_2=C(Cl)CH_2-$	H	128-131°C
153	4-Cl	phenyl	H	O	$CH_2=C(Cl)CH_2-$	H	128-133°C
154	4-Cl	phenyl	C_2H_5	O	$(CH_3)_3CCH_2-$	H	83-87°C
155	4-CH_3	phenyl	CH_3	O	$CH_3CH=CHCH_2-$	H	1.5272
156	4-Cl	phenyl	H	O	$(CH_3)_3CCH_2-$	H	97-103°C
157	4-Cl	phenyl	CH_3	O	$(CH_3)_3CCH_2-$	H	122-126°C
158	3-CH_3O, 4-Cl	phenyl	H	O	CH_3	H	160-164°C
159	2-CH_3O, 5-Cl	phenyl	H	O	CH_3	H	163-166°C
160	—	styryl	H	O	CH_3	H	145-152°C
161	4-Cl	phenyl	CH_3	O	$CH\equiv CC(CH_3)_2-$	H	1.5262
162	4-Cl	phenyl	C_2H_5	O	$CH\equiv CC(CH_3)_2-$	H	1.5188
163	4-NO_2	phenyl	CH_3	O	$CH_2=CHCH_2-$	H	94-97°C
164	4-NO_2	phenyl	CH_3	O	$CH\equiv CCH_2-$	H	100-105°C

* Confirmed by nuclear magnetic resonance or infrared spectroscopy.

It is clear that the classes of herbicidal agents described and illustrated herein are characterized as effective herbicides exhibiting such activity. The degree of this herbicidal activity varies among specific compounds and among combinations of specific compounds within the classes. Similarly, the degree of activity to some extent varies among the species of plants to which a specific herbicidal compound or combination may be applied. Thus, selection of a specific herbicidal compound or combination to control undesirable plant species readily may be made. Within the present invention the prevention of injury to a desired crop species in the presence of a specific compound or combination may be achieved. The beneficial plant species which can be protected by this method is not intended to be limited by the specific crops employed in the examples.

The herbicidal compounds employed in the utility of this invention are active herbicides of a general type. That is, the members of the classes are herbicidally effective against a wide range of plant species with little or no discrimination between desirable and undesirable species. The method of controlling vegetation comprises applying an herbicidally effective amount of the herein described herbicidal compounds to the area or plant locus where control is desired.

An herbicide as used herein means a compound which controls or modifies the growth of vegetation or plants. Such controlling or modifying effects include all deviations from natural development; for example, killing, retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, dwarfing and the like. By "plants" it is meant germinant seeds, emerging seedlings, and established vegetation, including the roots and above-ground portions.

The terms "herbicide antidote" or "antidotal amount" are meant to describe the effect which tends to counteract the normal injurious herbicidal response that the herbicide might otherwise produce. Whether it is to be termed a remedy, interferant, protectant, or the like, will depend upon the exact mode of action. The mode of action is varied, but the effect, which is desirable, is the result of the method of treating the seed, soil or furrow in which a crop is planted. Hitherto, there

have been no systems employing the antidote of the present invention which have been satisfactory for this purpose.

Broadly considered, this invention additionally relates to herbicidal compositions and methods comprising an active thiolcarbamate or haloacetanilide herbicide compound and a non-phytotoxic antidotally effective amount of a carbamate or thiolcarbamate or inorganic or organic salt of a combination or thiolcarbamate of an aryl sulfonylurea having 5 to 12 carbon atoms, inclusive, said carbamate, thiolcarbamate or salt thereof being antidotally active with said herbicide compound.

As alternative modes of action, the compounds of this invention may interfere with the normal herbicidal action of the thiolcarbamate-type, thiolcarbamate sulfoxide-type or haloacetanilide-type or other herbicides to render them selective in their action. The observation noted with the presence of the herein described antidote is a decrease in phytotoxicity with respect to various crops. The phytotoxicity is otherwise observed when various thiolcarbamates, thiolcarbamate sulfoxides or haloacetanilide herbicides are used for weed control. Whichever mode of action is present, the corresponding beneficial and desirable effect is the continued herbicidal effect of the thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide against weed species present with the crop, with the accompanying selective decreased herbicidal effect on desired crop species. This advantage and utility will become more apparent hereinafter.

Evaluation and Testing Procedure

Stock solutions of the herbicides were prepared by diluting the requisite amount of each herbicide in water. The solution compositions and application rates and methods are summarized in Table II.

Test Procedures and Results

TABLE II

Herbicide Stock Solution

Herbicide Name	Composition: Herbicide (mg)	Composition: Water or Acetone (ml)	Application: ml/flat	Application: lb/acre	Application: Method[1]
VERNAM® S-propyl N,N-dipropyl thiocarbamate	296	400	5	1.0	PPI
	370	370	5	1.25	PPI
	167	150	5	1.5	PPI
	148	100	5	2.0	PPI
	370	200	5	2.5	PPI
	296	100	5	4	PPI
	1480	400	5	5	PPI
	1776	400		6	PPI
TILLAM® S-propyl butyl-ethylthiocarbamate	296	100	5	4	PPI
RO-NEET® S-ethyl N-cyclo-hexyl-N-ethyl thio-carbamate	740	250	5	3	PPI
SUTAN® S-ethyl diisobutyl-thiocarbamate	2960	500	5	3	PPI
LASSO® 2-chloro-2'-6'-diethyl-N-(methoxy-methyl) acetanilide	7656	700 (1:1)[3]	L.S.T.[2]	2.5	PES
TERIDOX® 2-chloro 2'-methyl-N-(methoxyethyl) acet-anilide	1050	700 (1:1)[3]	L.S.T.[2]	1	PES
HERBICIDE A S-isobutyl-N,N-diethylthiocarbamate	148	50	5	4	PPI
	222	50	5	6	PPI
HERBICIDE B S-butyl isobutyl-ethylthiocarbamate	296	100	5	4	PPI
	284	50	5	6	PPI
HERBICIDE C S-butyl propyliso-propylthiocarbamate	296	100	5	4	PPI
	222	50	5	6	PPI

TABLE II (Cont'd)

Herbicide Stock Solution

Herbicide Name	Composition: Herbicide (mg)	Composition: Water or Acetone (ml)	Application: ml/flat	Application: lb/acre	Application: Method[1]
HERBICIDE D 2-t-butyl,6-methyl-N-n-propoxymethyl-chloroacetanilide	37	20	2	1	PES
HERBICIDE E 2-t-butyl,6-methyl-N-ethoxymethyl-chloroacetanilide	37	20	2	1	PES
HERBICIDE F S-propyl N,N-diiso-butylthiocarbamate	111	50	5	1	PPI
HERBICIDE G S-butyl N,N-diiso-butylthiocarbamate sulfoxide	111	50	5	3	PPI

[1]Method

PES = Pre-emergence surface application

PPI = Pre-plant incorporation

[2]L.S.T. = Linear spray table

3 = (Water:acetone)

Stock solutions of each antidote compound were prepared at the desired concentration by diluting the requisite amounts of each antidote in acetone. The compositions and rates for each method of application are summarized in Table III.

TABLE III

Antidote Stock Solutions

Antidote: Aryl Sulfonylureas

Composition		Application		
Antidote (mg)	Acetone (ml)	ml/flat	lb/acre	Method[1]
93	15	0.3	1.0	IF
93	15	1.5	5.0	IF
37	100	5.0	0.5	PPI
74	100	5.0	1.0	PPI
148	100	5.0	2.0	PPI
93	25	5.0	5.0	PPI
16	5	1/2 ml/10 grams seed		0.015 ST
16	2.5	1/2 ml/10 grams seed		0.03 ST
50	4	1/2 ml/10 grams seed		0.06 ST
100	4	1/2 ml/10 grams seed		0.125 ST
25	1/2	1/2 ml/10 grams seed		0.25 ST
200	2	1/2 ml/10 grams seed		0.5 ST

IF = In-furrow surface application
PPI = Pre-plant incorporation of herbicide and antidote as a tank mix
ST = Seed treatment

All of the soil used in the tests described herein was loamy sand soil treated with 50 parts per million (ppm) each of a commercially available fungicide, cis-N[trichloromethyl)-thio]-4-cyclohexene-1,2-dicarboximide, and 18-18-18 fertilizer, which contains 18% by weight equivalent each of nitrogen, phosphorus pentoxide, and potassium oxide.

The thiocarbamate herbicides were applied to the soil by pre-plant incorporation (PPI) either alone or with the antidote as a tank mix. The acetanilide and pyrrolidinone herbicides were applied by atomizing the herbicide, or herbicide/antidote tank mix, to the soil surface of seeded flats.

The antidote compounds were applied by PPI, pre-emergence surface (PES), seed treatment (ST), and in-furrow (IF) methods of application.

For in-furrow antidote applications, a one pint (473 cubic centimeters) sample of soil from each planting flat was removed and retained. After leveling and furrowing the soil, seeds of the crop or weed species were planted 1/2 inch (1.27 centimeter). Each flat was divided in half by a wooden barrier. A stock solution of the antidote was atomized directly onto the exposed seeds and soil in the open furrow on one side of the barrier. The seeds in the entire flat were then covered with the previously removed soil. The antidotally untreated sections of flats were compared for observed differences which would indicate lateral movement of the antidote through the soil.

For the pre-plant incorporation method the herbicide and the antidote of each test group were incorporated into the soil either each alone or together as a tank mix using a five gallon rotary mixer.

Pre-emergence surface (PES) application involves spraying the soil-covered seeds after planting.

All flats were placed on greenhouse benches where temperature was maintained between 70 and 90°F (21 to about 32°C). The flats were watered by sprinkling as needed to assure good plant growth.

Control flats contained crops treated with herbicides only at the various rates and method of application.

Injury ratings were taken four weeks after application of the antidote. The effectiveness of the antidote was determined by visual comparison of injuries to crops and weeds in the control and test flats to those in untreated flats.

The treated crops initially screened for diminution of herbicidal injury were milo (MO), wheat (WH), cotton (CT), rice (RC), barley (BA), corn (CN) and soybeans (SOY). Those compounds which showed substantial crop injury reduction were further tested at reduced rates. The herbicides and antidote compositions were then screened on at least two weed species. The weed species tested for control included watergrass (WG) (Echinochloa crusgalli), foxtail (FT) (Setaria viridis), wild oats

(WO) (Avena fatua), shattercane (SC) (Sorghum bicolor), Johnsongrass (JG) (Sorghum halepense), wild oats (WO) (Avena fatua), nutsedge (NS) (Cyperus esculentus), crabgrass (CG) (Digitaria sanguinalis) (L.) Scop, mustard (MD) (Brassica juncea), signalgrass (SG) (Brachiaria platyphylla, and cockleburr (CB) (Xanthium pensylvanicum).

KEY TO TABLE IV

Antidotes

Compound numbers in this table corresponds to the numbers and their chemical description in Table I.

Application:
- IF = In-furrow surface
- PPI-TM = Pre-plant incorporated of herbicide and antidote as a tank mix
- PPI = Pre-plant incorporation of herbicide or antidote as indicated
- PES = Pre-emergence surface
- ST = Seed treatment

Rates are shown in pounds per acre based on the surface area of the flat.

Reported result = Treated/untreated (T/U)

TABLE IV

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
1	5 IF	1 PPI VERNAM	CT	40/60		
			BA	50/70		
	5 IF	6 PPI VERNAM	SOY	40/60		
	1 IF	6 PPI VERNAM	SOY	30/45	FT	100/100
					CG	95/95
	5 IF	6 PPI VERNAM	SOY	10/45	FT	100/100
					CG	95/95
2	5 IF	1 PPI VERNAM	BA	40/60		
	5 IF	6 PPI VERNAM	SOY	0/50		
	1 IF	6 PPI VERNAM	SOY	20/40	WG	100/100
					FT	100/100
	2 PPI-TM	6 PPI VERNAM	SOY	40/65	WG	100/100
					FT	100/100
3	5 IF	1 1/4 PPI VERNAM	MO	40/100		
	5 IF	6 PPI VERNAM	CN	50/90		
	1 IF	3 PPI RO-NEET	MO	40/75	FT	80/80
					SC	95/95
	5 PPI-TM	6 PPI VERNAM	SOY	15/60	WG	100/100
					FT	100/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
3	1 PPI-TM	6 PPI VERNAM	SOY	0/60	WG	100/100
					FT	100/10
	5 IF	3 1/2 PES LASSO	MO	45/95	WG	100/100
			RC	70/100		
			BA	60/70		
	5 IF	1 PES TERIDOX	MO	35/100	WG	100/100
			WH	60/70		
			BA	60/80		
			CN	85/100		
	.125 ST	5 PPI VERNAM	SOY	10/40	WG	100/100
	5 PPI-TM	6 PPI VERNAM	SOY	35/70	WG	100/100
	5 PPI-TM	4 PPI VERNAM	SOY	10/60	WG	100/100
	.015% ST	2.5 PPI VERNAM	SOY	20/40		
	5 IF	3 PPI RO-NEET	MO	40/75	WG	95/95
					FT	95/95
	2.0 PPI-TM	6 PPI A	SOY	10/45		
	.5 PPI-TM	4 PPI B	SOY	0/35	WG	75/75
	.5 PPI-TM	6 PPI C	SOY	0/15	WG	95/95
	.3 PPI-TM	3 PPI F	SOY	0/30	WG	100/100
	1 PPI-TM	3 PPI F	SOY	0/30	WG	100/100
	2 PPI-TM	3 PPI F	SOY	0/30	WG	100/100
	1 PPI-TM	3 PPI G	SOY	0/10	WG	100/100
	.5 PES-TM	1 PES D	SOY	0/15	WG	100/100
	2 PES-TM	1 PES E	SOY	10/25	WG	100/100
	.5 PPI-TM	4 PPI TILLAM	SOY	0/47	WG	95/95
	1 PPI-TM	4 PPI TILLAM	SOY	0/47	WG	95/95
4	5 IF	1 1/4 PPI VERNAM	BA	50/90		
	5 IF	6 PPI VERNAM	SOY	20/50		
	5 IF	3 PPI RO-NEET	MO	40/75	FT	80/80
					SC	95/95
	5 PPI-TM	6 PPI VERNAM	SOY	35/70	WG	100/100
	5 IF	3 PPI RO-NEET	MO	45/75	WG	10
					FT	100/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
5	5 IF	1 1/4 PPI VERNAM	MO	60/100		
	1 IF	3 PPI RO-NEET	MO	45/75	WG	95/95
					FT	95/95
6	5 IF	6 PPI VERNAM	CN	40/90		
	5 PPI-TM	6 PPI VERNAM	SOY	45/70	WG	100/100
					FT	97/97
	5 IF	3.5 PES LASSO	MO	40/95	WG	100/100
			WH	55/70		
			BA	55/70		
	5 IF	3 PPI RO-NEET	MO	35/75	WG	95/95
					FT	95/95
7	5 IF	1 1/4 PPI VERNAM	WH	50/85		
	5 IF	6 PPI VERNAM	CN	60/90		
8	5 IF	6 PPI VERNAM	CN	70/90		
			SOY	40/60		
	1 IF	5 PPI VERNAM	SOY	20/60	WG	100/100
					FT	90/90
9	5 IF	6 PPI VERNAM	CN	50/90		
	5 PPI-TM	6 PPI VERNAM	SOY	55/70	WG	100/100
	5 IF	3 PPI RO-NEET	MO	30/75	WG	85/95
					FT	95/95
10	1 PPI-TM	6 PPI SUTAN	CT	10/50	NS	90/90
					JG	100/100
	1 PPI-TM	1 1/4 PPI VERNAM	CT	20/30	WG	100/100
					FT	100/100
11	5 IF	6 PPI VERNAM	CN	20/90		
	2 PPI-TM	4 PPI VERNAM	SOY	25/60	WG	100/100
12	5 IF	1 1/4 PPI VERNAM	MO	55/95		
	5 IF	6 PPI VERNAM	CN	0/95		
	2 PPI-TM	4 PPI VERNAM	SOY	30/60	WG	100/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
13	5 IF	1 1/4 PPI VERNAM	WH	50/90		
	5 PPI-TM	4 PPI VERNAM	SOY	35/60	WG	100/100
14	5 IF	6 PPI VERNAM	CN	0/95		
	5 PPI-TM	4 PPI VERNAM	SOY	35/60	WG	100/100
15	5 IF	1 1/4 PPI VERNAM	MO	50/100		
	5 IF	5 PPI VERNAM	CN	50/90		
	5 PPI-TM	4 PPI VERNAM	SOY	35/60	WG	100/100
16	5 IF	6 PPI VERNAM	SOY	20/60		
	5 PPI-TM	4 PPI VERNAM	SOY	35/60	WG	100/100
17	5 PPI-TM	4 PPI VERNAM	SOY	40/60	WG	100/100
18	5 IF	1 1/4 PPI VERNAM	MO	50/100		
	5 IF	5 PPI VERNAM	CN	65/95		
			SOY	30/95		
19	5 IF	5 PPI VERNAM	CN	80/95		
20	5 IF	1 1/4 PPI VERNAM	MO	40/100		
			CN	65/95		
22	5 IF	1 1/4 PPI VERNAM	MO	50/100		
	5 IF	5 PPI VERNAM	CN	70/95		
			SOY	25/50		
23	5 IF	5 PPI VERNAM	SOY	25/50		
24	5 IF	1 1/4 PPI VERNAM	MO	50/100		
26	5 IF	5 PPI VERNAM	CN	70/95		
27	2 PPI-TM	4 PPI TILLAM	SOY	5/47	WG	9[illegible]
28	5 IF	1.25 PPI VERNAM	MO	25/95		
	5 IF	5 PPI VERNAM	CN	30/99		
29	5 IF	1.25 PPI VERNAM	MO	25/95		
	5 IF	5 PPI VERNAM	CN	50/99		
	5 PPI-TM	4 PPI VERNAM	SOY	25/55	WG	95/95
30	5 IF	1.25 PPI VERNAM	MO	35/95		
	5 IF	5 PPI VERNAM	CN	20/99		
	4 PPI-TM	4 PPI VERNAM	SOY	15/55	WG	100/100
					FT	100/100
31	5 IF	5 PPI VERNAM	CN	10/99		
	4 PPI-TM	4 PPI VERNAM	SOY	20/55		

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
32	5 IF	1.25 PPI VERNAM	MO	95/95		
	5 IF	5 PPI VERNAM	CN	20/99		
	4 PPI-TM	4 PPI VERNAM	SOY	30/55		
33	5 IF	1.25 PPI VERNAM	MO	25/95		
	5 IF	5 PPI VERNAM	CN	45/99		
	5 PPI-TM	4 PPI VERNAM	SOY	35/55	WG	95/95
	2 PPI-TM	4 PPI VERNAM	SOY	35/55	WG	100/100
					FT	100/100
34	5 IF	1.25 PPI VERNAM	MO	30/95		
	5 IF	5 PPI VERNAM	CN	35/99		
	5 PPI-TM	4 PPI VERNAM	SOY	35/55	WG	95/95
35	5 IF	1.25 PPI VERNAM	MO	45/95		
	5 IF	5 PPI VERNAM	CN	20/99		
	5 PPI-TM	4 PPI VERNAM	SOY	30/55	WG	95/95
36	5 IF	5 PPI VERNAM	SOY	40/60		
	1 PPI-TM	4 PPI VERNAM	SOY	25/40		
37	5 IF	1.25 PPI VERNAM	MO	70/95		
38	5 IF	1.25 PPI VERNAM	BA	70/85		
39	5 IF	1.25 PPI VERNAM	MO	30/95		
			CT	40/60		
	5 IF	5 PPI VERNAM	CN	25/90		
40	5 IF	5 PPI VERNAM	CN	60/90		
41	5 IF	1.25 PPI VERNAM	MO	20/95		
	5 IF	5 PPI VERNAM	CN	50/90		
42	5 IF	5 PPI VERNAM	CN	70/90		
43	5 IF	1.25 PPI VERNAM	MO	60/100		
	5 IF	5 PPI VERNAM	SOY	35/65		
	5 PPI-TM	4 PPI VERNAM	SOY	50/80		
44	5 IF	1.25 PPI VERNAM	MO	35/97		
	5 IF	5 PPI VERNAM	CN	30/90		
	5 PPI-TM	3 PPI RO-NEET	MO	50/70	WG	50/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
45	1 PPI-TM	2 PPI VERNAM	SOY	50/80	WG	80/80
					FT	55/55
					CB	0/0
					MD	25/25
46	5 PPI-TM	4 PPI VERNAM	SOY	45/55		
47	5 IF	1.25 PPI VERNAM	MO	70/90		
			RC	65/95		
	5 IF	5 PPI VERNAM	SOY	45/60		
48	5 IF	1.25 PPI VERNAM	RC	30/95		
49	5 IF	1.25 PPI VERNAM	MO	20/90		
	5 IF	5 PPI VERNAM	CN	40/90		
50	5 IF	1.25 PPI VERNAM	RC	60/95		
	5 IF	5 PPI VERNAM	SOY	40/60		
51	5 IF	1.25 PPI VERNAM	MO	45/90		
			BA	30/90		
	5 IF	5 PPI VERNAM	CN	30/90		
52	5 IF	5 PPI VERNAM	SOY	60/90		
	5 PPI-TM	4 PPI VERNAM	SOY	0/60	WG	100/100
	1 PPI-TM	2 PPI VERNAM	SOY	10/20	WG	75/95
					FT	60/77
					CB	70/35
					SG	20/50
	2 PPI-TM	4 PPI VERNAM	SOY	0/43	WG	100/100
					FT	100/100
					CB	75/38
					SG	100/73
53	5 PPI-TM	4 PPI VERNAM	SOY	40/55	WG	95/95
	2 PPI-TM	2 PPI VERNAM	SOY	35/80	WG	80/80
					FT	55/55
					MD	25/25
	4 PPI-TM	2 PPI VERNAM	SOY	0/80	WG	80/80
					FT	55/55
					MD	
54	5 IF	5 PPI VERNAM	SOY	30/70		
	1 PPI-TM	4 PPI VERNAM	SOY	15/40	WG	100/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
55	5 IF	5 PPI VERNAM	SOY	30/70		
56	5 IF	5 PPI VERNAM	SOY	40/70		
	2 PPI-IM	4 PPI VERNAM	SOY	25/40	WG	100/100
57	5 IF	1.25 PPI VERNAM	RC	70/90		
	5 IF	5 PPI VERNAM	CN	70/90		
58	5 IF	1.25 PPI VERNAM	MO	65/95		
			RC	35/70		
	5 PPI-IM	4 PPI VERNAM	SOY	0/60		
59	5 IF	5 PPI VERNAM	SOY	60/90		
60	5 IF	1.25 PPI VERNAM	MO	75/90		
61	5 IF	1.25 PPI VERNAM	WH	70/90		
	5 IF	5 PPI VERNAM	SOY	55/90		
62	5 IF	5 PPI VERNAM	SOY	65/90		
	2 PPI-IM	4 PPI VERNAM	SOY	40/60	WG	100/100
63	5 IF	1.25 PPI VERNAM	MO	20/95		
	5 IF	5 PPI VERNAM	CN	40/90		
			SOY	55/90		
	5 PPI-IM	4 PPI VERNAM	SOY	25/60	WG	100/100
	1 PPI-IM	4 PPI VERNAM	SOY	25/60	WG	100/100
64	5 IF	1.25 PPI VERNAM	MO	30/95		
			WH	35/90		
			RC	10/70		
			BA	30/80		
	5 IF	5 PPI VERNAM	CN	30/90		
65	5 IF	1.25 PPI VERNAM	WH	60/90		
	5 IF	5 PPI VENRAM	SOY	50/90		
66	5 IF	1.25 PPI VERNAM	MO	45/97		
	5 IF	5 PPI VERNAM	CN	60/90		
67	5 IF	1.25 PPI VERNAM	MO	40/97		
	5 IF	5 PPI VERNAM	CN	40/90		
68	5 IF	1.25 PPI VERNAM	MO	15/97		
	5 IF	5 PPI VERNAM	CN	80/90		
69	5 IF	1.25 PPI VERNAM	MO	30/97		
	5 IF	5 PPI VERNAM	CN	75/90		
	5 PPI-IM	4 PPI VERNAM	SOY	40/60	WG	100/100

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
70	5 IF	1.25 PPI VERNAM	MO	50/97		
	5 PPI-TM	4 PPI VERNAM	SOY	50/60	WG	100/100
71	5 IF	5 PPI VERNAM	SOY	50/60		
	5 PPI-TM	4 PPI VERNAM	SOY	40/55	WG	95/95
72	2 PPI-TM	4 PPI VERNAM	SOY	40/60		
	1 PPI-TM	4 PPI VERNAM	SOY	40/60		
73	5 IF	1.25 PPI VERNAM	MO	60/95		
	5 IF	5 PPI VERNAM	CN	40/95		
	4 PPI-TM	4 PPI VERNAM	SOY	15/50	WG	100/100
	1 PPI-TM	4 PPI VERNAM	SOY	10/50	WG	100/100
74	5 IF	1.25 PPI VERNAM	MO	35/95		
			RC	60/100		
	5 IF	5 PPI VERNAM	CN	35/95		
			SOY	15/60		
	5 PPI-TM	4 PPI VERNAM	SOY	20/40	WG	100/100
					FT	100/100
	1 PPI-TM	4 PPI VERNAM	SOY	25/40	WG	100/100
					FT	100/100
75	5 IF	1.25 PPI VERNAM	MO	50/95		
	5 IF	5 PPI VERNAM	CN	35/95		
	4 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	100/100
76	5 IF	1.25 PPI VERNAM	MO	60/95		
	5 IF	5 PPI VERNAM	SOY	25/60		
	5 PPI-TM	5 PPI VERNAM	SOY	30/60	WG	100/100
					FT	85/85
77	5 IF	1.25 PPI VERNAM	MO	40/95		
	5 IF	5 PPI VERNAM	SOY	10/60		
78	5 IF	1.25 PPI VERNAM	MO	60/95		
			RC	65/100		
79	5 IF	1.25 PPI-VERNAM	MO	40/95		
	5 IF	5 PPI VERNAM	CN	60/95		

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
80	5 IF	1.25 PPI VERNAM	MO	40/95		
	5 IF	5 PPI VERNAM	CN	0/99		
	5 PPI-TM	4 PPI VERNAM	SOY	30/60	WG	100/100
81	5 PPI-TM	4 PPI VERNAM	SOY	15/50		
82	5 IF	5 PPI VERNAM	SOY	30/60		
83	5 IF	5 PPI VERNAM	CN	0/90		
			SOY	40/65		
84	5 IF	5 PPI VERNAM	CN	20/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/40	WG	100/100
					FT	100/100
85	5 IF	1.25 PPI VERNAM	MO	60/100		
	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
	2 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
86	5 IF	1.25 PPI VERNAM	MO	60/100		
	5 IF	5 PPI VERNAM	CN	50/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
	2 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
87	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
88	5 IF	5 PPI VERNAM	CN	15/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
	2 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
89	5 IF	5 PPI VERNAM	CN	15/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
90	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
91	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
92	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
93	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
94	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
	2 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
95	5 IF	5 PPI VERNAM	CN	20/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
96	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	[illegible]
	1 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
97	5 IF	5 PPI VERNAM	CN	0/90		
	2 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
98	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
99	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/50	WG	85/85
	1 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
100	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
	1 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
101	5 IF	5 PPI VERNAM	CN	0/90		
	2 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
102	5 IF	5 PPI VERNAM	CN	0/90		
	2 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
103	5 IF	5 PPI VERNAM	CN	0/90		
	2 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	85/85
104	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	35/50	WG	85/85
105	5 IF	5 PPI VERNAM	CN	0/90		
			SOY	10/65		
	5 PPI-TM	4 PPI VERNAM	SOY	30/50	WG	85/85
106	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	25/50	WG	[illegible]
107	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	35/50	WG	85/85

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
108	5 IF	5 PPI VERNAM	CN	0/90		
109	5 IF	1.25 PPI VERNAM	MO	65/100		
	5 IF	5 PPI VERNAM	CN	0/90		
110	5 IF	1.25 PPI VERNAM	MO	75/100		
	5 IF	5 PPI VERNAM	CN	0/90		
111	5 IF	5 PPI VERNAM	CN	0/90		
112	5 IF	1.25 PPI VERNAM	MO	65/100		
	5 IF	5 PPI VERNAM	CN	0/90		
113	5 IF	5 PPI VERNAM	CN	0/90		
			SOY	40/65		
114	5 IF	5 PPI VERNAM	CN	0/90		
115	5 IF	1.25 PPI VERNAM	BA	55/85		
	5 IF	5 PPI VERNAM	CN	0/90		
	5 PPI-TM	4 PPI VERNAM	SOY	20/40	WG	90/90
116	5 IF	1.25 PPI VERNAM	MO	70/100		
	5 IF	5 PPI VERNAM	CN	70/90		
117	5 IF	5 PPI VERNAM	SOY	30/40		
118	5 IF	5 PPI VERNAM	SOY	25/50		
119	5 IF	1.25 PPI VERNAM	BA	55/80		
120	5 IF	1.25 PPI VERNAM	MO	40/98		
			BA	45/80		
	5 IF	5 PPI VERNAM	CN	60/90		
121	5 IF	5 PPI VERNAM	SOY	35/68		
122	5 IF	5 PPI VERNAM	SOY	30/68		
123	5 IF	1.25 PPI VERNAM	MO	55/93		
	5 IF	5 PPI VERNAM	CN	50/90		
			SOY	45/68		
124	5 IF	1.25 PPI VERNAM	MO	50/93		
	5 IF	5 PPI VERNAM	CN	15/90		
			SOY	20/68		
	5 PPI-TM	3 PPI VERNAM	SOY	25/40		

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
125	5 IF	5 PPI VERNAM	SOY	25/68		
	4 PPI-IM	2 PPI VERNAM	SOY	0/20	WG	90/90
					CB	35/30
	2 PPI-IM	2 PPI VERNAM	SOY	0/20	WG	90/90
					CB	30/30
126	5 IF	1.25 PPI VERNAM	MO	40/100		
			RC	20/90		
			BA	10/95		
	5 PPI-IM	1 PPI VERNAM	RC	30/95	WG	90/90
	1 PPI-IM	1 PPI VERNAM	RC	50/95	WG	90/90
	4 PPI-IM	3 PPI VERNAM	SOY	20/40	WG	90/90
127	5 IF	1.25 PPI VERNAM	CT	20/40		
	5 IF	5 PPI VERNAM	CN	40/75		
			SOY	30/45		
	5 PPI-IM	4 PPI VERNAM	SOY	40/70	WG	100/100
					FT	85/85
	1 PPI-IM	4 PPI VERNAM	SOY	30/70	WG	100/100
					FT	85/85
128	5 IF	5 PPI VERNAM	CN	0/75		
			SOY	20/45		
	5 PPI-IM	4 PPI VERNAM	SOY	40/70	WG	100/100
					FT	85/85
	1 PPI-IM	4 PPI VERNAM	SOY	40/70	WG	100/100
					FT	85/85
129	5 IF	1.25 PPI VERNAM	MO	70/100		
	5 IF	5 PPI VERNAM	CN	50/75		
			SOY	20/45		
	5 PPI-IM	4 PPI VERNAM	SOY	30/70	WG	100/100
					FT	85/85
	2 PPI-IM	4 PPI VERNAM	SOY	35/70	WG	100/100
					FT	85/85
	4 PPI-IM	3 PPI VERNAM	SOY	30/40	WG	

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
130	5 IF	1.25 PPI VERNAM	BA	30/95		
	5 PPI-TM	4 PPI VERNAM	SOY	10/70	WG	100/100
					FT	85/85
	2 PPI-TM	3 PPI VERNAM	SOY	20/40	WG	90/90
131	5 IF	5 PPI VERNAM	SOY	40/65		
132	5 IF	5 PPI VERNAM	SOY	30/60		
	5 PPI-TM	3 PPI VERNAM	SOY	15/30	WG	90/90
133	5 IF	1.25 PPI VERNAM	MO	60/90		
			BA	60/90		
134	5 IF	1.25 PPI VERNAM	RC	20/70		
135	5 IF	1.25 PPI VERNAM	RC	10/70		
			BA	30/90		
136	5 IF	1.25 PPI VERNAM	MO	50/90		
			RC	25/70		
			BA	30/90		
	5 IF	5 PPI VERNAM	SOY	30/50		
	5 PPI-TM	3 PPI VERNAM	SOY	15/40	WG	95/95
	2 PPI-TM	3 PPI VERNAM	SOY	15/40	WG	95/95
137	5 IF	1.25 PPI VERNAM	MO	40/90		
			WH	45/75		
			BA	25/90		
	5 IF	5 PPI VERNAM	CN	45/90		
138	5 IF	1.25 PPI VERNAM	MO	35/90		
			WH	25/75		
			RC	10/70		
			BA	20/90		
139	5 IF	1.25 PPI VERNAM	MO	55/90		
	5 IF	5 PPI VERNAM	SOY	20/30		
140	5 IF	5 PPI VERNAM	SOY	20/30		
	5 PPI-TM	3 PPI VERNAM	SOY	20/40	WG	95/95
141	5 IF	5 PPI VERNAM	SOY	30/55		
142	5 IF	1.25 PPI VERNAM	BA	40/65		
	5 IF	5 PPI VERNAM	SOY	35/55		

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
143	5 IF	1.25 PPI VERNAM	MO	60/100		
144	5 IF	1.25 PPI VERNAM	BA	35/65		
145	5 IF	1.25 PPI VERNAM	CT	35/45		
146	5 IF	5 PPI VERNAM	CN	30/90		
			SOY	40/60		
	5 PPI-TM	4 PPI VERNAM	SOY	35/85	WG	95/95
	2 PPI-TM	4 PPI VERNAM	SOY	55/85	WG	95/95
147	5 IF	5 PI VERNAM	SOY	30/60		
148	5 IF	1.25 PPI VERNAM	MO	55/90		
			CT	20/35		
149	5 IF	1.25 PPI VERNAM	MO	65/90		
	5 PPI-TM	4 PPI VERNAM	SOY	55/85	WG	95/95
150	5 IF	5 PPI VERNAM	SOY	20/60		
151	5 IF	5 PPI VERNAM	SOY	35/60		
152	5 IF	5 PPI VERNAM	SOY	35/60		
153	5 IF	1.25 PPI VERNAM	MO	55/90		
	5 IF	5 PPI VERNAM	SOY	15/60		
	5 PPI-TM	4 PPI VERNAM	SOY	50/85	WG	95/95
154	5 IF	5 PPI VERNAM	SOY	55/75		
155	5 IF	5 PPI VERNAM	SOY	15/60		
156	5 IF	5 PPI VERNAM	SOY	40/60		
157	5 IF	1.25 PPI VERNAM	RC	40/75		
	5 IF	5 PPI VERNAM	SOY	30/60		
158	5 IF	1.25 PPI VERNAM	MO	35/95		
	5 IF	5 PPI VERNAM	SOY	40/60		
159	5 IF	1.25 PPI VERNAM	WH	60/90		
			BA	30/80		
	5 IF	5 PPI VERNAM	CN	20/95		
160	5 IF	1.25 PPI VERNAM	MO	25/90		
	5 IF	5 PPI VERNAM	CN	25/95		
161	5 IF	5 PPI VERNAM	CN	50/95		
			SOY	40/65		

TABLE IV (Cont'd)

Compound Number	Antidote Rate & Method	Herbicide Rate & Method	Crop	Result	Weed	Result
162	5 IF	1.25 PPI VERNAM	WH	50/90		
			RC	30/80		
	5 IF	5 PPI VERNAM	CN	30/95		
			SOY	30/65		
163	5 IF	5 PPI VERNAM	SOY	45/65		
164	5 IF	5 PPI VERNAM	SOY	30/65		

The antidote compounds and compositions of the present invention can be used in any convenient form. Thus, the antidote compounds can be formulated into emulsifiable liquids, emulsifiable concentrates, liquid, wettable powder, powders, granular or any other convenient form. In its preferred form, an herbicidal antidote compound in a non-phytotoxic quantity with respect to the crop is admixed with a selected herbicide and incorporated into the soil prior to or after planting the seed. It is to be understood, however, that the herbicides can be incorporated into the soil and thereafter the antidote compound can be incorporated into the soil. Moreover, the crop seed itself can be treated with a non-phytotoxic quantity of the compound and planted into the soil which has been treated with herbicides, or untreated with the herbicide and subsequently treated with the herbicide. The addition of the antidote compound does not effect the herbicidal activity of the herbicides except to render the activity selective with respect to beneficial crops.

The amount of antidote compound present can range between about 0.01 to about 30 parts by weight of antidote compound described herein per each part by weight of herbicide. The exact amount of antidote compound will usually be determined on economic ratios for the most effective amount usable. It is understood that a non-phytotoxic quantity of antidote compound with respect to a particular crop will be employed in the herbicidal compositions described herein.

Formulations

The compounds and compositions can be formulated in the same manner in which herbicides are generally formulated. The object of the formulation is to apply the compounds and compositions to the locus where

control is desired by a conventional method. The "locus" may include soil, seeds, seedlings, and vegetation.

The active herbicidal ingredient of a formulation will generally be such that its application rate will be within the range of 0:01 to 50 lb/A (0.0112 to 56 k/ha). The antidote compound which may be formulated separately or together with the herbicide will generally comprise about 0.01 to about 30 parts by weight of the herbicide.

Formulations will generally contain several additives. Among these are some inert ingredients, diluent carriers, organic solvents, water, oil and water, water in oil emulsions, carriers of dusts and granules, and surface active wetting, dispersing, and emulsifying agents.

Fertilizers, e.g., ammonium nitrate, urea and superphosphate, may also be included.

Aids to rooting and growth, e.g., compost, manure, humus, sand etc., may likewise be included.

Dusts are free-flowing powder compositions containing the herbicidal compound impregnated on a particulate carrier. The particle size of the carriers is usually in the approximate range of 30 to 50 microns. Examples of suitable carriers are talc, bentonite, diatomaceous earth, and pyrophyllite. Anti-caking and anti-static agents can be added, if desired. The composition generally contains up to 50% of active ingredient. Dusts, like liquid compositions, can be applied by spraying from boom and hand sprayers or airplanes.

Wettable powders are finely divided compositions comprising a particulate carrier impregnated with the herbicidal compound and additionally containing one or more surface active agents. The surface active agent promotes rapid dispersion of the powder in aqueous medium to form stable, sprayable suspensions. A wide variety of surface active agents can be used, for example, long chain fatty alcohols and alkali metal salts of the sulfated fatty alcohols; salts of sulfonic [illegible]; esters of long chain fatty acids; and polyhydric alcohols, in which the alcohol groups are free, omega-substituted polyethylene glycols of

relatively long chain length. A list of surface active agents suitable for use in agriculture formulations can be found in Wade Van Valkenburg, Pesticide Formulations, (Marcel Dekker, Inc., N.Y., (1973) at pages 79-84.

Granules comprise the herbicidal composition impregnated on a particulate inert carrier having a particle size of about 1 to 2 millimeters in diameter. The granules can be made by spraying a solution of the active ingredient in a volatile solvent onto the granule carrier. Suitable carriers in preparation of granules include clay, vermiculite, sawdust, granular carbon, etc.

The herbicidal compositions can also be applied to the soil in the form of a solution in a suitable solvent. Solvents frequently used in herbicidal formulations include kerosene, fuel oil, xylene, petroleum fractions with boiling ranges above xylene, and aromatic petroleum fractions rich in methylated naphthalenes.

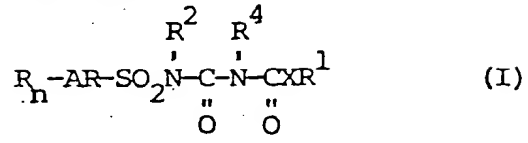
Emulsifiable concentrates consist of an oil solution of the herbicide along with an emulsifying agent. Prior to use the concentrate is diluted with water to form a suspended emulsion of oil droplets. The emulsifiers used are usually a mixture of anionic and nonionic surfactants. Other additives such as spreading agents and stickers can be included in the emulsifiable concentrate.

The compounds and compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein.

It is not necessary that the compounds and compositions be admixed with the soil particles. After application by the above discussed methods, they may be distributed below the surface to a depth of at least one-half inch by conventional means such as discing, dragging, or mixing.

WHAT IS CLAIMED IS:

1. Compounds having the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive;

R is lower alkyl having 1 to 4 carbon atoms, inclusive; lower alkoxy having 1 to 4 carbon atoms; lower alkylthio having 1 to 4 carbon atoms, inclusive; halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl;

R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl;

R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2-6 carbon atoms, and phenyl;

R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and

AR is phenyl, benzyl, naphthyl, pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine and tribenzylamine.

2. A compound according to Claim 1 in which R is halogen, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl.

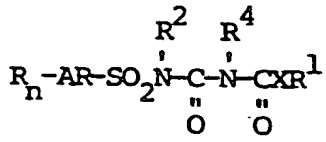
3. A compound according to Claim 1 in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic bases selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

4. The method of protecting a crop from injury due to at least one thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide, comprising

a) applying to the crop seed prior to planting, a non-phytotoxic antidotally effective amount of a compound corresponding to the following formula I; or

b) preplant incorporation in the soil in which said crop is to be planted, a non-phytotoxic antidotally effective amount of a compound of the formula I; or

c) applying in-furrow to the seed and soil in which said crop is to be planted, a non-phytotoxic antidotally effective amount of a compound corresponding to the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive;

R is lower alkyl having 1 to 4 carbon atoms, inclusive; lower alkoxy having 1 to 4 carbon atoms; lower alkylthio having 1 to 4 carbon atoms, inclusive; halogen, trifluormethyl, cyano, nitro, lower alkyl sulfonyl;

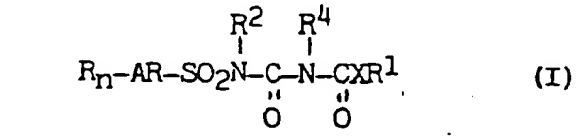
R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive; lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl; R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2 to 6 carbon atoms, and phenyl;

R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive; haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive; 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive; phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and

AR is phenyl, benzyl, naphthyl, pyridyl or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic base salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenmediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N,-dialkyl hydrazine, morpholine, and tribenzylamine.

5. The method according to Claim 4 in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group, said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic base salts selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

6. A herbicidal composition comprising at least one thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide active herbicide and an antidotally effective amount of a compound therefore corresponding to the formula I



$$R_n\text{-}AR\text{-}SO_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}N\text{-}\underset{\underset{O}{\|}}{C}XR^1 \qquad (I)$$

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive,

R is lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxy having 1 to 4 carbon atoms;
lower alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl acylamido;

R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorphenyl;

R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having from 2 to 6 carbon atoms, and phenyl;

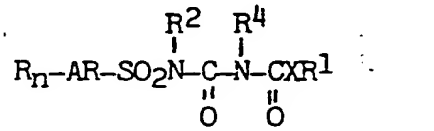
R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, phenyl and alkyl substituted phenyl wherein the alkyl moiety has 1 to 4 carbon atoms, inclusive; and

AR is phenyl, benzyl, naphthyl, pyridyl, or styryl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

7. A herbicidal composition according to Claim 6 in which R is halogen, n is 1, 2 or 3, AR is phenyl, R^4 is hydrogen, R^2 is hydrogen, X is oxygen and R^1 is lower alkyl.

8. A herbicidal composition according to Claims 6 or 7 in which the salt is selected from the group consisting of sodium, potassium, ammonium, the aliphatic ammonium group, said aliphatic containing from 1 to 18 carbon atoms, quaternary organic bases, phosphonium bases, sulfonium bases and oxonium bases, organic base salts selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

9. The method of increasing the resistance of crop plant seed to injury from at least one herbicidally active thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide, comprising applying to the surface of said seed a coating of an antidotally effective, but substantially non-phytotoxic amount of a compound corresponding to the formula I



(I)

in which X is oxygen or sulfur; n is an integer 0 to 3, inclusive;

R is lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxy having 1 to 4 carbon atoms;

lower alkylthio having 1 to 4 carbon atoms, inclusive, halogen, trifluoromethyl, cyano, nitro, lower alkyl sulfonyl

R^4 is hydrogen and lower alkyl having 1 to 4 carbon atoms, inclusive, lower alkoxyalkyl having 2 to 6 carbon atoms, inclusive, phenyl and chlorophenyl;

R^2 is hydrogen, lower alkyl having 1 to 4 carbon atoms, alkoxyalkyl having 2 to 6 carbon atoms, and phenyl;

R^1 is lower alkyl having 1 to 4 carbon atoms, inclusive, alkenyl having 3 to 6 carbon atoms, inclusive, alkynyl having 3 to 6 carbon atoms, inclusive, haloalkyl having 1 to 4 carbon atoms, inclusive, alkoxyalkyl having 2 to 6 carbon atoms, inclusive, 1-phenyl propenyl, benzyl, chlorobenzyl, haloalkenyl having 3 to 6 carbon atoms, inclusive, alkyl having 1 to 4 carbon atoms, inclusive, substituted phenyl; and

AR is phenyl, benzyl, naphthyl, pyridyl, or stylyl; and the inorganic base salts sodium, potassium, ammonium and other inorganic salts and organic base salts thereof selected from the group consisting of aniline, p-toluidine, benzylamine, allylamine, diallylamine, triallylamine, alkylamine, dialkylamine, trialkylamine, tetraalkyl ammonium, ethylaminoethyl, alkanolamine, dialkanolamine, trialkanolamine, quinoline, isoquinoline, ethylenediamine, benzyltrialkyl ammonium, choline, hydrazine, N,N-dialkyl hydrazine, morpholine, and tribenzylamine.

10. The method of protecting soybean plants from injury due to at least one thiolcarbamate or haloacetanilide comprising applying to the soil a herbicidal composition according to Claim 6 or Claim 7.

11. The method of Claim 10 in which said thiolcarbamate herbicide compound is selected from EPTC, S-ethyl diisobutyl thiolcarbamate, S-propyl dipropyl thiolcarbamate, S-2,3,3,-trichloroallyl diisopropyl thiolcarbamate, S-ethyl cyclohexyl ethyl thiolcarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate, S-4-chlorobenzyl diethyl thiolcarbamate and combinations thereof.

12. A herbicidal composition comprising an active thiolcarbamate, thiolcarbamate sulfoxide, or haloacetanilide herbicide compound and a non-phytotoxic antidotally effective amount of a carbamate or thiolcarbamate of an aryl sulfonylurea, having 5 to 12 carbon atoms, inclusive, said carbamate or thiolcarbamate being antidotally active with said herbicide compounds.

13. A herbicidal composition comprising an active thiolcarbamate, thiolcarbamate sulfoxide or haloacetanilide herbicide compound and a non-phytotoxic, antidotally effective amount of an inorganic or organic salt of a carbamate or thiolcarbamate of an aryl sulfonylurea, having 5 to 12 carbon atoms, inclusive, said salt being antidotally active with said herbicide compound.